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CITATION:

Sakurada, Ichiro ...[et al]. Chemical Structure of Poly (Vinyl Alcohol)-Methyl Methacrylate Graft Coplymer Prepared by Pre-Irradiatflon Techniqu (Special issue on Physical, Chemical and Biological Effects of Gamma Radiation, X). Bulletin of the Institute for Chemical Research, Kyoto University 1969, 47(1): 49-57

ISSUE DATE:

1969-03-31

URL:

http://hdl.handle.net/2433/76265

Bull. Inst. Chem. Res., Kyoto Univ., Vol. 47, No. 1, 1969

# Chemical Structure of Poly(Vinyl Alcohol)-Methyl Methacrylate Graft Copolymer Prepared by Pre-Irradiation Technique

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*Received January 17, 1969*

Poly(vinyl alcohol) (PVA) films were pre-irradiated in air to a dose of $1.0\times10^6$r and graft copolymerization of methyl methacrylate (MMA) onto the films was carried out in methanol solution of the monomer which contained trichloroethylene to control the branch length. The graft copolymer was isolated from the grafting product by alternate extraction of the homoPMMA and the ungrafted PVA. The PVA part of the isolated graft copolymer was acetylated to make better the compatibility between the backbone and the branch and then fractionated into 13 fractions by addition of *n*-hexane to benzene solution of the acetylated graft copolymer. After acetyl groups in the fractionated graft copolymers were converted to hydroxyl groups again, 1,2-glycol bonds of backbone PVA was cleaved with periodic acid to separate the branch from the backbone polymer. The molecular weights of fractionated graft copolymers and the separated branches were measured by osmometry after acetylation of the PVA part. The chemical composition of each fraction was determined by hydrolysis of acetyl groups in the graft copolymer. From the result obtained, it was found that the number of branch is only one per each graft copolymer molecule, while the backbone is formed from several mother PVA molecules, which are crosslinked. The chain length of homopolymer formed in the interior of the film was found to be approximately equal to that of the branch.

## INTRODUCTION

Although a large number of studies have been done on the radiation-induced graft copolymerization, most of them have been restricted merely on the methods to prepare various graft copolymers and to increase the extent of grafting reaction, and quite little effort[1~3] has been directed towards a systematic investigation to characterize the graft copolymers formed. It seems, however, very important to obtain a knowledge of the chemical structure of the graft copolymers, not only to learn an accurate picture of the mechanism of the grafting reaction, but also to evaluate their physical properties. Therefore, we initiated a series of studies to characterize the graft copolymers prepared by radiation and catalytic techniques and to obtain graft copolymer with well-defined structure for studies of their physico-chemical properties.

In the present investigation, poly(vinyl alcohol) (PVA) was chosen as the substrate polymer from the main reasons that the conditions of the graft copoly-

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merization onto PVA have been studied extensively in our laboratory[4], and that grafted branches can be separated away readily from the main chain of the substrate by cleaving 1, 2-glycol bonds which are present by about 1~2 mole% in the PVA molecule obtained by the conventional polymerization of vinyl acetate.

A previous study[5] aimed to characterize the graft copolymer prepared by immersing pre-irradiated films of PVA in methanol solution of methyl methacrylate (MMA) has demonstrated that each graft copolymer has one extraordinarily long branch with a molecular weight of several millions. If the molecular weight of graft copolymer is so high, it becomes considerably difficult to characterize the graft copolymer in detail by ordinary methods. Therefore, the graft copolymer sample reported in this paper was prepared in the presence of trichloroethylene (TCE) as a chain transfer agent to shorten the length of the branches. The other condition of grafting was the same as described previously[5].

## EXPERIMENTAL

### 1. Graft Copolymerization

PVA used as the substrate polymer was a fractionated one with a molecular weight of 88,000. Films of 0.05 mm thickness prepared from this PVA by a casting method were irradiated in the presence of air at room temperature with gamma-rays from a CO-60 source. The dose rate and the total dose were $9.52 \times 10^4$ r/hr and $1.0 \times 10^6$ r, respectively. The irradiated films were transferred into an ampoule, the inside air was evacuated, degassed monomer solution was allowed to enter through a breakable seal into the ampoule and then sealed. The composition of the monomer solution was as follows[6] : MMA : TCE=2 : 1 (by mole), (MMA+TCE) : methanol=2 : 3 (by vol.). 6.704 g of PVA films were employed for 500 ml of monomer solution. The chain transfer constant of TCE was found previously to be $2.1 \times 10^{-4}$.[6] The graft copolymerization was carried out at 50°C for 64.5 hrs under incessant rotation of the sealed ampoule.

### 2. Extraction of Homopolymer

The homoPMMA formed in the outer solution and occluded loosely in the interior of the grafted films was removed by extraction with acetone at room temperature for 1 day. The selective extraction was then alternately repeated with boiling acetone for the homoPMMA and boiling water for the ungrafted PVA in a flask equipped with a condenser. The solvent was exchanged frequently for the freshly distilled one during the extractions. The usual Soxhlet extractor was not used in the present work, since extraction could be performed more effectively by this method, as Brockway[7] pointed out, too. When the amount of extractable polymers became relatively small, the residue was dissolved in dimethyl formamide (DMF) and precipitated into methanol to obtain flocky precipitate, which was again subjected to alternate extraction. This re-precipitation and extraction cycle was repeated till no more homoPMMA or PVA was extracted. The shape of residue before dissolution in DMF was still film-like, and X-ray diffraction photograph of the residue showed relatively sharp rings due to the crystalline

part in PVA.

### 3. Acetylation and Hydrolysis

The PVA backbone of the isolated graft copolymer was acetylated completely with acetic anhydride-pyridine (1 : 2) mixture at 110°C for 16 hrs. Under the assumption that all hydroxyl groups of PVA have been acetylated, vinyl acetate content of the graft copolymer may be calculated from hydrolysis of the acetylated copolymer. The hydrolysis was carried out under the condition[8] that only the acetyl groups were selectively hydrolyzed, while methacrylate groups in the graft copolymer remained unreacted. The con dition of the hydrolysis was as follows. About 50 mg of the sample was dissolved in 40 ml acetone followed by addition of N/4 methanolic NaOH, and the solution was kept at 30°C for 3 days. The amount of hydrolyzed groups was determined by back-titration.

### 4. Fractionation and Measurement of Molecular Weight

The acetylated graft copolymer was fractionated by the fractional precipitation method, that is, by dropwise addition of *n*-hexane to 1 % benzene solution at 30°C. This solvent-precipitant system was adopted, because clear phase-separation occurred, while in other ones tried by preliminary experiments satisfactory phase-separation did not occur. After each fractionated graft copolymer was purified by re-precipitation, its molecular weight was determined by osmometry by the use of a modified Zimm-Myerson osmometer or "501 High-Speed Membrane osmometer" manufactured by Mechrolab Inc. The measurements were carried out for benzene solutions at 30°C, covering polymer concentrations from $2\times10^{-3}$ to $11\times10^{-3}$ g/ml. The chemical compositions of the fractionated graft copolymers were determined by hydrolysis of the PVAc part of the graft copolymers.

### 5. Separation of Branch

After the PVAc part of the graft copolymer was converted to PVA again, the grafted branches were separated from the backbone by cleaving 1, 2-glycol bonds of the hydrolyzed graft copolymer with periodic acid in dimethyl sulfoxide at 30°C for 3 hrs. It was confirmed by a preliminary experiment that neither degradation nor hydrolysis of PMMA chain took place during the treatment with periodic acid. Short PVA chains attached to ends of the separated PMMA branches were acetylated again and the molecular weights of the separated branches were determined by osmometry in benzene at 30°C.

## RESULTS

### 1. Isolation of Graft Copolymer

As the removal of the homoPMMA and the ungrafted PVA was carried out as vigorously as possible by alternate extraction and re-precipitation, the possibility of inclusion of these free polymers in the residue may be regarded to be virtually zero or extremely low.

The result of the extraction is summarized in Table 1. It can be seen that

32.3 % of the PVA substrate participates in the grafting reaction. The percent grafting and the graft efficiency calculated after the conventional, that is, first extraction of homoPMMA alone were 299 % and 42.5 %, respectively, whereas the complete extraction of the homoPMMA decreased the percent grafting and the graft efficiency to remarkably low values such as 41.2 % and 5.8 %. The hydroxyl group content in the isolated graft copolymer estimated from the extraction result was 64.1 mole%, which was in good agreement with 66.4 mole% calculated from hydrolysis of the acetylated graft copolymer.

Table 1. Extraction of homoPMMA and ungrafted PVA.

| | Total weights of polymers before extraction, A (g) | Total weights of extracted polymers, B (g) | Weights in graft copolymer (g) | $\frac{A-B}{B}\times 100$ |
|---|---|---|---|---|
| PVA | 6.704 | 4.539 | 2.165 | 32.3 |
| PMMA | 47.162 | 44.407 | 2.755 | 5.8 |

The viscosity-average degrees of polymerization (DP) of extracted homopolymer were plotted against the extraction time in Fig. 1. It is seen that the homoPMMA with higher DP is less easily extracted. The same, but less noticable tendency is also observed in the case of extraction of the ungrafted PVA.

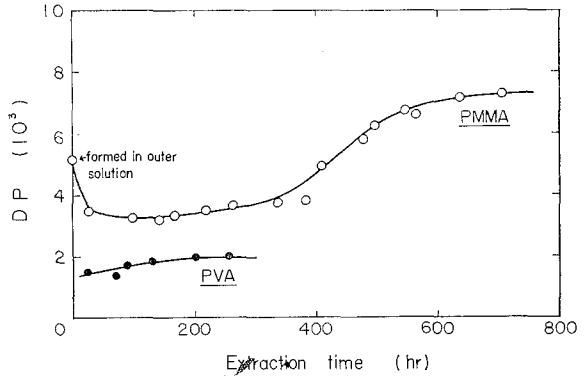


Fig. 1. DP of the extracted homoPMMA and the ungrafted PVA.

Some measurements were carried out to check whether the extracted polymers were actually pure homoPMMA or pure PVA. It was found from the infrared spectroscopy that all the extracted polymers contained no detectable amount of the graft copolymer except the polymers obtained by the last extractions. For these polymers it was found from the acetylation reaction to be neither pure PMMA nor pure PVA, although the degree of impurity was very low. Namely, only 5 mole% of the polymer obtained by the last extraction with acetone, and as much as 95 mole% of the polymer obtained by the last extraction with boiling water could be acetylated.

## 2. Fractionation of Acetylated Graft Copolymer

Only few studies[9,10] have been done, up to date, on the fractionation of pure

graft copolymers. One of the main reasons may be that it is much complicated compared to that of homopolymers. For instance, it is seldom that a clear liquid-liquid phase-separation which is essential for fractional precipitation, is observed for graft copolymers. In the present case, however, the phase-separation occurred quite smoothly when *n*-hexane was added as a precipitant to benzene solution of the acetylated graft copolymer, probably because the backbone polymer and the branch polymer became completely compatible as a result of the acetylation of PVA backbone. On the other hand, when water was added at 30°C till to cloud point to the acetone or DMF solution of the acetylated graft copolymer, the solution remained turbid at least for three days without occurrence of phase-separation.

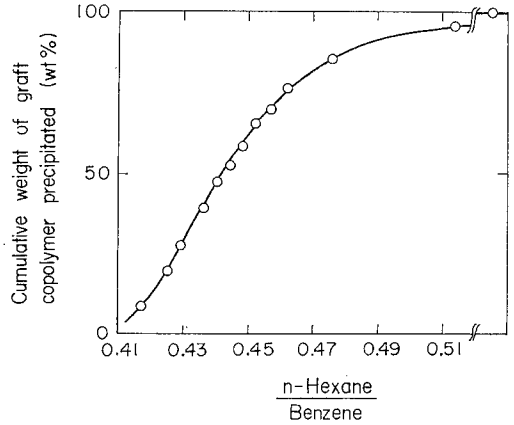


Fig. 2. Fractional precipitation curve of the PVAc-MMA graft copolymer.

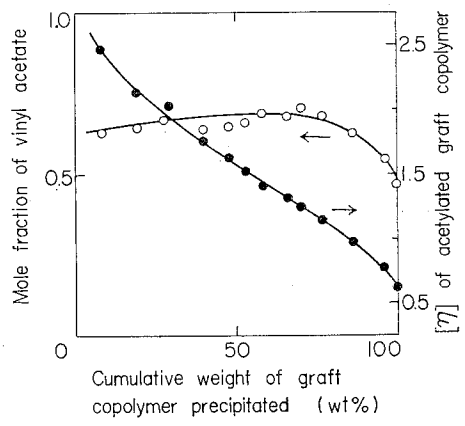


Fig. 3. Chemical composition and $[\eta]$ of the fractionated PVAc-MMA graft copolymer in benzene at 30°C.

The cumulative weight of graft copolymers precipitated was plotted against the ratio of *n*-hexane to benzene in Fig. 2, which shows a smooth precipitation curve. The final fraction was recovered by evaporation of the solvent from the residuary solution. Fig. 3 shows the limiting viscosity number $[\eta]$ in benzene at 30°C and the chemical composition of the fractions, as a function of the cumulative weight of the graft copolymer precipitated. As is obvious from Fig. 3, the composition of the fractions is nearly constant except two last fractions, while $[\eta]$ is decreased markedly, as the fractionation proceeds. The result demonstrates strongly that the graft copolymer is fractionated mainly by the difference in the molecular weight of the graft copolymer.

### 3. Molecular Weight of Fractions

Some examples of osmotic pressure measurements are shown in Fig. 4. For comparison, results measured by a modified Zimm-Myerson osmometer and by a High-Speed Membrane osmometer are given in Fig. 5. As can be seen, the agreement of data obtained by the two different osmometers is satisfactory, although the data obtained by the High-Speed Membrane osmometer are somewhat scattered. Also for other fractions, the same linearity held between the reduced

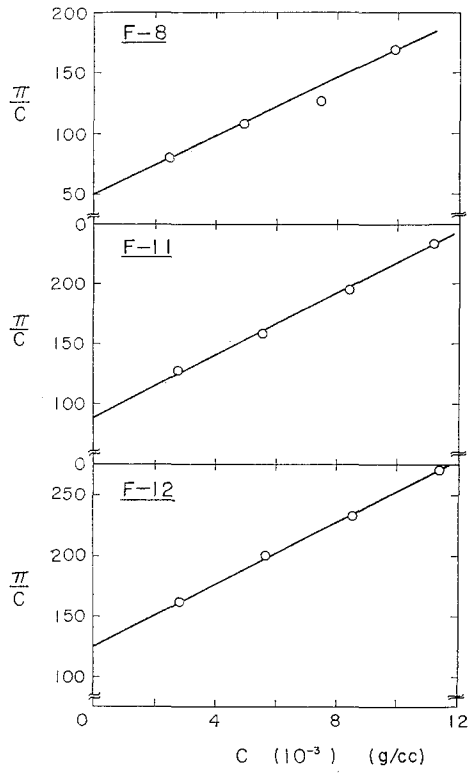


Fig. 4. Relationship between reduced osmotic pressures, $\pi/c$, and polymer concentrations for the several graft copolymers.

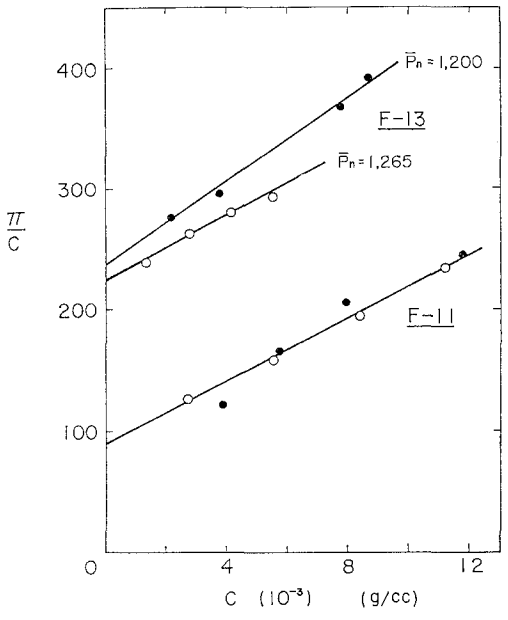


Fig. 5. Comparison of osmotic pressures measured by the modified Zimm-Myerson osmometer (○) and by the High-Speed Membrane osmometer (●).

osmotic pressure and the polymer concentration over a wide concentration range. The second virial coefficients ranged from $4.6\times10^{-4}$ to $5.2\times10^{-4}$ cm³·mole/g², being nearly equal to those for pure PMMA[11] and PVAc[12] reported in literatures.

If hydroxyl groups of PVA part in the graft copolymer are incompletely acetylated, it is possible for the graft copolymer molecules to associate in benzene. To examine this possibility, $[\eta]$ of the graft copolymer, PMMA and PVAc were measured in various solvents such as benzene, DMF and the benzene-methanol (95 : 5) mixture, in which the possible association by hydroxyl groups is supposed to be broken. As a results, it was confirmed that no appreciable association took place in the benzene solution, in other words, the graft copolymer was dissolved in benzene molecularly.

Molecular weights, $\bar{M}_n$, of the fractionated graft copolymers and the separated branches are listed in Table 2. As mentioned above, a short chain of PVA (or PVAc) may be attached to an end of the separated side-chain, but it was not considered at the estimation of molecular weight of the branch, because it must be negligibly short compared to that of the PMMA branch.

Table 2. Molecular weight and chemical composition of fractions.

| Fraction number | $\bar{M}_n$ ($10^5$) | | Chemical composition | | |
|---|---|---|---|---|---|
| | Acetylated graft copolymer | Separated branch | Wt. fraction | | mole fraction VAc |
| | | | MMA | VAc | |
| 1 | 13.13 | — | 0.404 | 0.596 | 0.631 |
| 2 | 11.18 | — | 0.394 | 0.606 | 0.641 |
| 3 | 10.26 | — | 0.371 | 0.629 | 0.664 |
| 4 | 8.87 | 3.27 | 0.396 | 0.604 | 0.639 |
| 5 | 8.05 | 2.96 | 0.390 | 0.610 | 0.645 |
| 6 | 7.04 | 2.69 | 0.378 | 0.622 | 0.657 |
| 7 | 6.43 | 2.28 | 0.347 | 0.653 | 0.686 |
| 8 | 4.94 | 2.15 | 0.360 | 0.640 | 0.674 |
| 9 | 4.21 | 1.94 | 0.339 | 0.661 | 0.694 |
| 10 | 3.61 | 1.78 | 0.391 | 0.609 | 0.644 |
| 11 | 3.43 | 1.33 | 0.409 | 0.591 | 0.626 |
| 12 | 2.58 | 1.15 | 0.499 | 0.501 | 0.538 |
| 13 | 1.18 | 0.82 | 0.571 | 0.429 | 0.466 |

## DISCUSSION

Based on the results obtained above, it is possible to discuss the chemical structure of the graft copolymer in detail. The number of branch and mother substrate PVA in one graft copolymer molecule can be calculated from the following equations:

$$\text{number of branch} = \frac{\bar{M}_n \text{ of branch part in graft copolymer}}{\bar{M}_n \text{ of separated branch}} = \frac{\left(\bar{M}_n \text{ of graft copolymer}\right) \times \left(\text{wt. fraction of MMA in graft copolymer}\right)}{\bar{M}_n \text{ of separated branch}} \quad (1)$$

Table 3. Number of branch and mother PVA in one fractionated graft copolymer.

| Fraction number | Weight fraction (%) | Number of branch | Number of mother PVA molecule |
|---|---|---|---|
| 1 | 9.31 | — | 5.69 |
| 2 | 11.72 | — | 4.92 |
| 3 | 8.64 | — | 4.71 |
| 4 | 12.70 | 0.93 | 3.89 |
| 5 | 8.46 | 0.94 | 3.56 |
| 6 | 5.44 | 1.01 | 3.19 |
| 7 | 6.42 | 1.02 | 3.05 |
| 8 | 7.53 | 1.21 | 2.34 |
| 9 | 4.65 | 1.35 | 2.03 |
| 10 | 5.61 | 1.38 | 1.66 |
| 11 | 7.51 | 1.49 | 1.47 |
| 12 | 7.70 | 1.80 | 0.94 |
| 13 | 4.38 | 2.13 | 0.38 |

$$\text{number of mother PVA} = \frac{\bar{M}_n \text{ of backbone part in graft copolymer}}{\bar{M}_n \text{ of mother PVA}} = \frac{\left(\bar{M}_n \text{ of acetylated graft copolymer}\right) \times \left(\text{wt. fraction of VAc in acetylated graft copolymer}\right)}{\bar{M}_n \text{ of acetylated mother PVA}} \quad (2)$$

The calculated values are given in Table 3. The molecular weight of starting PVA (88,000) was used as that of mother PVA throughout in every fraction. As is obvious from Table 3, it can be concluded that in most cases only one branch is grafted onto each backbone. This conclusion agrees with that of the previous study in our laboratory[5].

Table 3 denotes also that the backbone polymer of this graft copolymer is constructed from several mother PVA molecules which are crosslinked with each other. The strong evidence for the formation of crosslinking was obtained, when irradiated PVA was treated under the same condition as for the graft copolymerization except that methyl isobutyrate (MIB) was used as a model compound of MMA. In this experiment it was observed that DP of the PVA was increased during this treatment with MIB. It is highly possible that the cosslinking takes place more readily during the actual grafting, since the mobility of PVA chain may be enhanced greatly by the presence of the compounds such as PMMA and methanol. According to a study carried out afterwards it was found that unirradiated PVA films also become partially insoluble when heated at 80°C in methanol-TCE (1 : 1) mixture. Therefore it can be said that pre-irradiation is not necessary for formation of crosslinks among PVA molecules if TCE is present in PVA films at high temperature as 80°C. More intensive investigation is now being carried out on the crosslinking of PVA by TCE. It should be pointed out here that the amount of the grafted PVA would be decreased from 32.2% to about only 10%, if any crosslinking did not take place among the mother PVA molecules.

Fig. 6 shows the DP distribution curve of the graft copolymer together with that of the separated branch. It is seen from Fig. 6 that the DP distribution of the graft copolymer is expectedly broad, whereas that of the grafted branch is

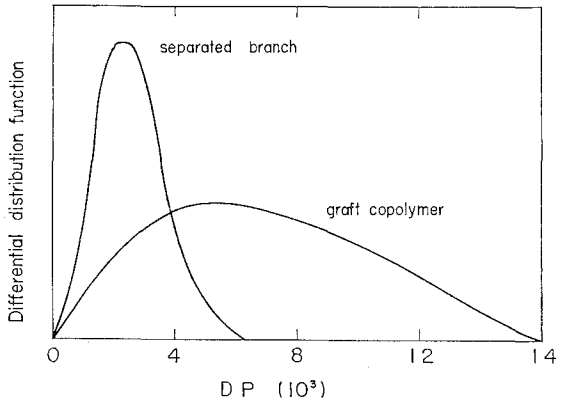


Fig. 6. DP distribution curves of the PVA-MMA graft copolymer and the grafted branch.

rather sharp. When the average number of mother PVA molecules in the whole graft copolymer is calculated from Fig. 6, it is found to be 2.1. It is interesting to note that, as is seen from the comparison of Fig. 1 with Fig. 6, the length of the homoPMMA formed in the substrate matrix can be considered to be approximately equal to that of the grafted branch, if it is taken into consideration that DP's of homopolymers are viscosity-average, while the latters are number-average.

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